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PATENT SPECIFICATION

700,608



Date of Application and filing Complete Specification Jan. 11, 1950.

No. 774/50.

Application made in United States of America on Jan. 12, 1949.

Complete Specification Published Dec. 9, 1953.

Index at acceptance :-- Classes 2(5), R3C(6: 8: 9: 10: 11: 12: 13), R3D(1: 2: 4: 5: 6: 11), R3M(2: 4), R3T2, R9C(6: 8: 9: 10: 11: 12: 13), R9(M: P: T2), R22C(6: 8: 9: 10: 11: 12: 13), R22(M: P: T2); 87(2), A1R3CX, A1R1-H(A: C2), A2C3; and 140, E1(A: H: M).

SEARCHED WRITTEN SPECIFICATION

SPECIFICATION NO. 700,608

By a direction given under Section 17(1) of the Patents Act 1949 this application proceeded in the name of Farbenfabriken Bayer Aktiengesellschaft, a German Body Corporate, of Leverkusen-Bayerwerk, Germany.

THE PATENT OFFICE,  
1st December, 1954

DB 70627/1(7)/3493 150 11/54

to a method for preparing . . .  
It is known that dicarboxylic acids and glycols can be converted by condensation into linear polyesters the molecular weight of which normally does not exceed 5000. These polyesters are either waxlike and low melting or highly viscous products which as such are not useful as plastics. It is only in exceptional cases, e.g. in the case of polyesters from sebacic acid and ethylene glycol that with the application of special methods of condensation high molecular weight polymers can be prepared which are capable of being spun from the melt and yield threads of a satisfactory degree of strength. On the other hand, these products are characterized by a low melting point which, as a rule, is below 100° C. whereby their practical application is at least strongly handicapped. Many attempts have been made to convert such products into high molecular weight polyesters in order to render them useful for all such applications to which related linear poly-condensation products are normally put. As far as we know, the first promising results in this direction have been achieved by causing polyesters of the character described to react with diisocyanates. We refer in this connection to French Patent 869,243 according to which high molecular, heat moldable products are obtained by causing diisocyanates and polyesters to react with each other in

there were ~~undesirable~~ <sup>undesirable</sup> products which besides valuable other qualities exhibit certain rubber-like properties. For this process there can be used various aliphatic and aromatic diisocyanates. As aliphatic isocyanates there should be mentioned: tetramethylene diisocyanate, 65 pentamethylene diisocyanate, hexamethylene diisocyanate and thioldipropyl diisocyanate. Of the aromatic series there may be mentioned the diisocyanates of the benzene series, e.g. phenylene diisocyanate, chlorophenylene diisocyanate, the toluylene diisocyanates and naphthylene diisocyanates. It is to be understood, however, that this rubberiness is restricted to the "vulcanized" state and not to the intermediate stages of condensation so that these products cannot serve as substitutes for rubber but constitute a new type of synthetic thermosetting highly polymeric product. One of the characteristics differences between natural rubber and synthetic rubberlike materials on the one hand and diisocyanate modified polyesters on the other hand resides in the fact that in the case of the latter the curing process starts from viscous or easily fusible products, "vulcanization" proceeding through all intermediate stages between the viscous and the "vulcanized" character, whereas rubber and rubberlike materials in the uncured state exhibit at the most certain thermoplastic properties. 80 85 90

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R22C(6: 8: 9: 10: 11: 12: 13), R22(M: P: T2); 87(2), A1R3CX,  
A1R14(A: C2), A2C3; and 140, E1(A: H: M).

## COMPLETE SPECIFICATION

### Polymeric Products Derived from Polyisocyanate-Modified Polyesters

We, FARRENFABRIKEN BAYER, a German Company recognised under German law, of 22c, Leverkusen Bayerwerk, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a new type of high molecular products which exhibit certain rubberlike properties and to a method for preparing such products.

It is known that dicarboxylic acids and glycols can be converted by condensation into linear polyesters the molecular weight of which normally does not exceed 5000. These polyesters are either waxlike and low melting or highly viscous products which as such are not useful as plastics. It is only in exceptional cases, e.g. in the case of polyesters from sebacic acid and ethylene glycol that with the application of special methods of condensation high molecular weight poly-

mers can be prepared which are capable of being spun from the melt and yield threads of a satisfactory degree of strength. On the other hand, these products are characterized by a low melting point which, as a rule, is below 100° C. whereby their practical application is at least strongly handicapped. Many attempts have been made to convert such products into high molecular weight poly-

esters in order to render them useful for all such applications to which related linear poly-condensation products are normally put. As far as we know, the first promising results in this direction have been achieved by causing polyesters of the character described to react with diisocyanates. We refer in this connection to French Patent 869,243 according to which high molecular, heat moldable products

are obtained by causing diisocyanates and polyesters to react with each other in

equivalent amounts. The reaction occurring between these products is due to the fact that the polyesters contain either hydroxyl or carboxyl end groups which react with the diisocyanate group while forming urethane or carbonamide groups, carbon dioxide being set free in the latter case. In a prior proposal, the diisocyanates were used in excess over that amount which is necessary for reacting with the hydroxyl and carboxyl end groups of the polyesters. In this manner there were obtained high molecular products which besides valuable other qualities exhibit certain rubber-like properties. For this process there can be used various aliphatic and aromatic diisocyanates. As aliphatic isocyanates there should be mentioned: tetramethylene diisocyanate, pentamethylene diisocyanate, hexamethylene diisocyanate and thiodipropyl diisocyanate. Of the aromatic series there may be mentioned the diisocyanates of the benzene series, e.g. phenylene diisocyanate, chlorophenylene diisocyanate, the toluylene diisocyanates and naphthylene diisocyanates. It is to be understood, however, that this rubberiness is restricted to the "vulcanized" state and not to the intermediate stages of condensation so that these products cannot serve as substitutes for rubber but constitute a new type of synthetic thermosetting highly polymeric product. One of the characteristic differences between natural rubber and synthetic rubberlike materials on the one hand and diisocyanate modified polyesters on the other hand resides in the fact that in the case of the latter the curing process starts from viscous or easily fusible products, "vulcanization" proceeding through all intermediate stages between the viscous and the "vulcanized" character, whereas rubber and rubberlike materials in the uncured state exhibit at the most certain thermoplastic properties.

It has been emphasized that the necessary cross-linking for rubberlike properties is due to a series of complicated reactions which are supposed to proceed as follows: the interaction of polyesters and an excess of diisocyanates over the amount which is equivalent to the polyester end groups results in a chain-lengthening, the units thus formed having isocyanate end groups. These terminal isocyanate groups react with water which results in a further union of two isocyanate groups by a urea linkage. In this manner a high molecular weight product is obtained. In the urea linkages the NH-groups are capable of interacting with further isocyanate groups thus giving rise to the formation of cross linkages and, in consequence thereof, of properties resembling those of natural or synthetic rubber in the vulcanized state. Only a small amount of water, about 0.2% is required to bring about this reaction. The water can be introduced by dropping into or by blowing steam onto the surface of the mix or, finally, by incorporating within the mix a salt which contains water of crystallization. The cured products obtained exhibit extraordinarily good properties, the most promising of which are tear resistance, ageing resistance, abrasion loss, fastness to ozone, and solvent resistance. These subjects have been published in Birs Final Report No. 35 1166 "Synthetic Rubber" Interrogation of Dr. Bayer and Dr. Roelig of I.G. Farbenindustrie Aktiengesellschaft, Leverkusen, in UK. on 1st and 2nd August 1946.

40 Products of the character described



whereas the remaining part of the isocyanate end groups might react with the 85 NH-groups thus formed, with cross-linking. We wish to emphasize, however, that the course of reaction has not been cleared up as yet. It is the more obscure as in general the hydrogen of urethane 90 groups, is not capable of reacting with isocyanates, at least under the conditions to be applied here and as the diisocyanate modified polyester likewise contains urethane groups without showing any 95 remarkable tendency of cross-linking.

At any rate, the use of glycols results in a curing process which is free from the disadvantage of bubble formation so that in accordance with the present invention 100 diisocyanate modified polyesters can be worked, molded and cured according to every process which is adapted to the respective state of condensation. Besides that, our new process is superior to the 105 prior known water process in that it

though distinguished by excellent mechanical properties suffer from certain disadvantages chief among which consists in the use of water as curing agent. Reaction of isocyanates with water to form ureas 45 is accompanied by the splitting off of carbon dioxide which forms bubbles in the mix. The bubbles must be prevented either by allowing the carbon dioxide to escape or by the application of pressure 50 thus keeping the carbon dioxide dissolved in the mix. Formation of bubbles could not be prevented, however, in the case of all such processing operations where pressure cannot be applied and the carbon 55 dioxide has no chance to escape. This is true, for instance, of the casting process referred to above.

This is the more embarrassing as the casting method involves a considerable 60 saving of time and expense when compared with the usual rubber processing and molding.

It is the object of our present invention to do away with these disadvantages and 65 to build up a diisocyanate modified polyester which can be satisfactorily worked and molded according to all methods which are adapted to the various intermediate stages of condensation including 70 the casting. Other objects of our invention will be apparent from the following specification and claims.

Our invention primarily consists in the use as curing agent for diisocyanate modified polyesters of glycols. The curing effect which is brought about by glycols might be due to the fact that part of the isocyanate end groups are tied together in the following manner:—

80

renders possible the modifying of the cured product by a suitable choice of glycol within very wide limits, in the first place as to the degree of softness. This will be explained in detail in the 110 following description and examples.

The linear polyesters which are starting materials for our present invention are made from at least one saturated dicarboxylic acid or from a hydroxy carboxylic 115 acid, optionally in mixture with a small amount of an aromatic or an unsaturated dicarboxylic acid, and at least one glycol optionally in mixture with a small amount of polyfunctional amine or an amino 120 alcohol. As acids there will be mentioned: malonic acid, succinic acid, adipic acid, the methyladipic acids, carbonic acid, dihydromuconic acid, thiadipropionic acid, diethylether-dicarboxylic acid, sebacic 125 acid, suberic acid and higher dicarboxylic acids.

As glycols there will be mentioned:

ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, 1,3-butylene glycol, 1,4-butylene glycol, 1,6-hexane diol, the methyl hexane-1,6-diols, 1,4-butene diol,  
 5 diethylene glycol, thiodiglycol, 2,2-dimethyl-1,3-propylene glycol. Hydroxy carboxylic acids can also be used in the preparation of polyesters, provided however, that the tendency thereof of linear  
 10 polycondensation is stronger than the tendency of ring formation and that sufficient glycols are present to secure formation of hydroxyl end groups. Moreover, mixtures of various acids and glycols can  
 15 be used, mixed polyesters being obtained thereby. Other bifunctional reactants which are complementary to the acids or glycols can be used in amounts up to 10% by weight of the respective acid or  
 20 glycol. As examples there are mentioned compounds containing aromatic nuclei, such as phthalic acid or terephthalic acid, unsaturated dicarboxylic acids such as maleic acid, aromatic or aliphatic di-  
 25 amines, for instance, phenylene diamines, naphthylene diamines, piperazine, ethylene diamine as well as amino alcohols, for instance, the amino propanols and the hydroxyethylanilines. Polycondensation  
 30 of the reactants is effected by heating to 100—250° C. Care must be taken that, owing to a slight excess of glycols and to sufficiently long heating, the polyester has practically no acid value. The OH-  
 35 value must be between about 20 and about 80, preferably between 40 and 60. That corresponds to a percentage of OH-groups of 0.6—2.4, preferably 1.2—1.8 by weight. Prior to the reaction with diisocyanates the polyesters thus obtained must be freed from water by heating to 100—150° C. in vacuum or by introducing inert gases at the same temperature. Among the acids preference is given to  
 40 adipic acid, and among the glycols to ethylene glycol and 1,2-propylene glycol.  
 For converting the polyesters into the diisocyanate modification products there-  
 50 fore care must be taken that the diisocyanates are used in an amount such that the number of NCO groups is in excess of the number required to react with the OH-groups. The excess must be within the limits of 20—250%, preferably 50—100%, over the number necessary for combining with the OH-groups. Owing to the reac-  
 55 tion which occurs in this step the OH end groups of the polyesters are converted into NCO end groups. Moreover, depending on the excess of diisocyanate several poly-  
 60 ester units can be linked together. In the case of a smaller excess up to 3 units may be linked where as in the case of a larger excess no chain lengthening occurs at all.  
 65 In the case of an NCO group excess of

more than 100% there will even remain some free diisocyanate in the mix. Aromatic diisocyanates are preferred and among them those of the polycyclic series as they have a certain "spaciousness" 70 confer some rigidity to the structure and cause separation of the adjacent chains. In the first instance, naphthylene-1,5-diisocyanate is to be mentioned. Furthermore, the other naphthylene diisocyanates can also be used as well as diisocyanates of the diphenyl series, for instance, 3,3-dichloro-diphenyl-4'-diisocyanate, and the diisocyanates of the pyrene, fluorene and chrysene series. Reaction of 80 the polyester with the diisocyanate is performed at temperatures from 80 to 150° C. in the absence of moisture. With the evolution of heat, there occurs a slight increase in viscosity. Materials thus 85 obtained can be stored unchanged for a prolonged period of time. Owing to the high reactivity of the NCO end group, it is preferred, however, to proceed with the following steps without delay. 90

In the next step, the diisocyanate modified polyester thus formed is caused to react with a glycol in such a proportion that the excess of free NCO groups will, after reaction with the glycol, be reduced 95 to an amount which represents an amount of diisocyanate which is by weight at most 4% of the weight of the initial polyester. In this step, the same glycols can be used as in the case of preparing the polyesters. We wish to state, however, that in this case less valuable products will be obtained from ethylene glycol in comparison with its higher homologues, e.g. 1,4-butanediol or the 100 corresponding unsaturated derivatives such as butenediol or butinediol. Especially suitable are also cyclic glycols such as quinitol or the hexahydropyrocatechols. As further glycols there may be men- 110 tioned: glyceryl- $\alpha$ -monochlorhydrin, glycerine- $\alpha$ -alkyl ethers or glycerine- $\alpha$ -aryl ethers, xylylene glycols, or the Diels-Alder addition product of butenediol and anthracene. It is found that aliphatic gly- 115 cols will yield softer products whereas the use of cyclic glycols, especially those with aromatic rings, results in harder materials. Reactivity of the glycols also varies within a wide scope. 120

It is an important feature of our invention that the reactivity of the diisocyanates with the polyester as well as with the glycols, which are used in the last step, can be influenced by various means thus 125 adapting the reaction velocity to the processing method desired. Three different factors which accelerate or retard the reaction velocity are described:—  
 (a) A remarkable delay in the reactivity 130

of the isocyanate groups can be achieved by using acid reacting agents which are added to the polyester prior to reaction with the diisocyanates. In the first instance, there may be mentioned hydrogen chloride which can be used either in the gaseous state or, to the extent of a few drops per kilogram of the melt, in form of aqueous hydrochloric acid. Sulfur dioxide, boric acid, and also organic acids which may have remained in the polyester from its manufacture or may be added thereto at a later stage have a similar effect. Those products also proved successful which decompose into acids only upon heating, e.g. butadiene sulfone (which decomposes into butadiene and sulfur dioxide). Besides, a delaying effect is reached by fillers of an acid character, e.g. activated charcoal, prepared in an acid medium.

(b) A substantial acceleration of the curing reaction is achieved by adding an alkaline reagent such as tertiary organic bases to the mix subsequent to or together with the incorporation of the glycols. The accelerating effect of pyridine on the isocyanate reaction is known. We have found that a stronger effect is achieved by using basic catalysts such as hexahydrodimethylaniline, methylpiperidine, dimethylpiperazine, tribenzylamine or tetramethyldiaminodipropylether. These catalysts are preferably used in quantities of 0.5 to 0.01% of the mix. Similar effects are achieved by using polyesters containing basic groups in chemical combination.

(c) We have further found that the technically prepared polyesters often considerably vary as to their reactivity towards diisocyanates. This phenomenon might be due to impurities having a catalytic effect or to unchanged glycols which adhere to the polyester. These anomalies, however, can easily be avoided by washing the polyester with water or with an immiscible organic solvent, or by blowing an inert gas through the melt at a raised temperature for a prolonged period of time.

In some cases, especially on casting, it is often desirable to combine these various regulating factors, for instance, in such a way that interaction of the polyester with the diisocyanate is retarded by acids so as to obtain a stable mix and, later on, the curing is accelerated by adding basic catalysts. In this manner, the reaction velocity can be well adapted to the various processing methods.

Dyestuffs, softeners and fillers can be added to the mixes during all processing steps without any difficulties. As suitable softeners there may be mentioned phthalic

acid esters and aromatic sulfonamides. Sulfur containing softeners are particularly suitable, e.g. methylene-bis-thioglycollic acid butyl ester. As in the case of natural rubber some of the fillers give rise to improved mechanical properties of the cured products. This is true for instance, of titanium dioxide and, particularly, of carbon black which, in an amount of 3-15% by volume considerably improves the tear resistance of the material. These fillers are worked either into the polyester or into its diisocyanate modification products. On processing tough mixes of an advanced state of condensation the addition can also be performed on the roller.

In the following, several characteristic processing methods for our new products will now be described:—

#### A) PRESS MOLDING

The diisocyanate modified polyester is caused to react with the glycol at a temperature of 100-150° C. with strong agitation, and condensation is carried out until the mix which, in the beginning becomes more and more viscous is at last converted into crumbly or tough material. For this processing mechanical kneading machines are preferably used. For instance, the apparatus according to Werner and Pfeiderer. On the roller the crumbly material can easily be made into a sheet which, at a temperature between 120-170° C. can be pressed into plates or molded articles of any kind.

#### B) CASTING

The molten diisocyanate modified polyester is caused to react with an appropriate amount of glycol; that mixture is briefly and thoroughly mixed and is cast into the mold desired in the hot state, before condensation is complete. Mixing may preferably be performed in screw conveyors. For securing easy removal of the molded article from the mold the latter is provided with a protective coating. Such a protective coating may consist, for instance, of waxlike materials or also of silicone or inert water-soluble films such as water-soluble cellulose derivatives. The reaction mixture remains in the mold until it is solidified. For that purpose, the molds are preferably heated to temperatures of 60 to 150° C. By after-heating outside the mold, the articles thus obtained can often be improved as to their mechanical properties. A special casting process is the centrifugal casting according to which the still liquid condensation product is cast into rotating molds wherein it remains until it is solidified while the molds are continuously rotating. Tyres for cycles can be prepared in this way in a flat structure as well as in

a mold representing the final shape of the tyre with or without fabric. Casting can also be performed at rates of rotation below the usual speed of centrifuges, for instance at 200 r.p.m. When preparing tyres the condensation product is either cast onto textile or metal nettings or the latter are worked into the cast tread. In this way for instance, tyres for cycles can be prepared in a completely new way. The mechanical properties of the cured product are such as to allow one to prepare excellent tyres even without fabric, the tyres thus made being, moreover, distinguished by a very low rolling resistance. Besides, the liquid intermediate state of condensation may be used for the lining or embedding of textiles or metal cord. This process offers prospects for perfectly new methods of preparing elastic articles, all the more so, as adhesion of these articles to all kinds of material is generally extraordinarily good. It has proved to be successful in many cases to combine the casting process and the press molding process, for instance, in such a manner that the castings are removed from the mold before the reaction is completed and are then pressed into the final shape. Of course, this casting process also allows one to prepare sheets on a suitable surface. In this case, it is sometimes of advantage to dilute the batch by adding inert solvents, such as chlorohydrocarbons, esters or aromatic hydrocarbons. On heating the sheets the solvent is evaporated. Also dipped articles can be prepared from such solutions.

**C) EXTRUDING AND CALENDERING**

For this processing method it is necessary to carry out condensation of the diisocyanate modified polyester with the glycol up to an intermediate state which is between that used for the casting on the one hand and for press molding on the other hand. This condition is achieved by a combination of the following steps: for preventing sticking a small amount of hard paraffin or fatty acid derivatives is added to the mix. The temperature is to be kept low. Addition of fillers, for instance, carbon black, titanium dioxide or calcium silicate, improves the workability of the material. On observing these conditions an easily moldable material will be obtained which, preferably at temperatures between 40–100° C., can be extruded in an ordinary extruding machine to form threads, belts or tubes. Sheets can also be obtained on the calender according to this process. For completing the reaction these molded products are after heated, preferably after storing them for some time. As especially valuable properties of the sheets and tubes

thus obtained their excellent tear resistance and gas impermeability should be emphasized. Many of the products thus prepared also exhibit a low swelling property in organic solvents.

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**D) RECLAIMING**

The cured products obtained according to the processes A)—C) or scrap material can be reclaimed in a simple manner. The scrap material can easily be made again into a moldable sheet on the roller. Sheet formation and, especially the subsequent re-molding are facilitated if plasticizers, e.g. unmodified polyester or also diisocyanate modified polyester are added. In this way, molded articles will be prepared which still exhibit about 70–80% of the mechanical properties of the original material.

Another method of reclaiming consists in heating ground scrap material with steam and blending the stock thus obtained either with freshly condensed material (polymerization product obtained by polymerizing the diisocyanate-modified polyester with glycol) or with a desired quantity of diisocyanate and subsequently pressing while heating. Products prepared from material thus reclaimed are easily moldable and their quality is almost as good as that of products prepared from freshly condensed material.

Our invention is further illustrated by the following examples in which adipic acid may be replaced by any of those listed hereinabove under almost equal conditions without, however, being restricted thereto, the parts being by weight if not otherwise stated:—

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**EXAMPLE 1**

1000 parts of glycol adipic acid polyester of the OH-value 50 (corresponding to 1.5% OH) are dehydrated in a stirring vessel at a temperature of 130° C. and 110 under a pressure of 12 mm. The polyester is free from water as soon as formation of bubbles has stopped. While stirring 160 parts of 1,5-naphthylene diisocyanate are added at 130° C. a rise of temperature 115 to 142° C. being observed thereby. As soon as temperature drops 25 parts of finely powdered quinone are stirred into the mix. After a few minutes the mix becomes more and more viscous and, at last, viscosity increases to such an extent that 20 minutes later the stirrer is stopped owing to the material having been converted into a crumbly mass. On the roller the condensation product may be made 125 into a sheet and upon press molding at 150° C for 20 minutes the following figures are obtained:—

	Tensile strength - - - - -	384 kg/cm <sup>2</sup>
	Elongation at break - - - - -	600 %
	Permanent set - - - - -	3 %
	Tear resistance - - - - -	175 kg/cm <sup>2</sup>
5	Load at 300% elongation - - - - -	60 kg/cm <sup>2</sup>
	Hardness - - - - -	65 Shore degrees
	Resiliency - - - - -	59 % of height of fall attained by elastic rebound

If 300 parts of carbon black are added 10 to the polyester there are obtained products which exhibit the following properties:

15	Tensile strength - - - - -	321 kg/cm <sup>2</sup>
	Elongation at break - - - - -	478 %
	Permanent set - - - - -	12 %
	Tear resistance - - - - -	240 kg/cm <sup>2</sup>
20	Load at 300% - - - - -	109 kg/cm <sup>2</sup>
	Hardness - - - - -	80 Shore degrees
	Resiliency - - - - -	52 % of height of fall attained by elastic rebound

In this manner there can be made sheets of a thickness between 0.5 and several 25 centimetres and, moreover, various molded articles such as heels, soles, packings, buffers for cars, sandals, bottle rings, balls, e.g., golf balls, hockey balls, bandages, bicycle handles, foot rests, etc.

30 1,5-naphthylene diisocyanate can be substituted by isomeric 1,4- or 2,7-naphthylene diisocyanate.

In this example, 9.4 grams of naphthylene diisocyanate (molecular weight 210) 35 are required per 100 grams of the polyester having OH number 50, for reaction with all the OH groups. The use of 9.4 grams diisocyanate would produce no excess of the latter. According to the 40 Example, however, 16 grams of diisocyanate are used, and an excess of 6.6 grams of the latter remains. The 2.5 grams of quinone used in the final reaction reacts with NCO groups representing 45 4.53 grams of diisocyanate (only one NCO group per molecule is considered in the calculation since only this group is a free

75	Tensile strength - - - - -	239.7 kg/cm <sup>2</sup>
	Elongation at break - - - - -	545 %
	Permanent set - - - - -	3 %
	Tear resistance - - - - -	125 kg/cm <sup>2</sup>
	Load at 300% elongation - - - - -	34 kg/cm <sup>2</sup>
	Hardness - - - - -	62 Shore degrees
	Resiliency - - - - -	69 % of height of fall attained by elastic rebound

80 On using 20 parts of 1,4-butene diol ( $\text{OH} \cdot \text{CH}_2 \cdot \text{C}\equiv\text{C} \cdot \text{CH}_2 \cdot \text{OH}$ ), the following properties are obtained provided that the

85	Tensile strength - - - - -	320 kg/cm <sup>2</sup>
	Elongation at break - - - - -	640 %
	Permanent set - - - - -	6 %
	Tear resistance - - - - -	158 kg/cm <sup>2</sup>
90	Load at 300% elongation - - - - -	35 kg/cm <sup>2</sup>
	Hardness - - - - -	60 Shore degrees
	Resiliency - - - - -	70 % of height of fall attained by elastic rebound

ties provided that the other conditions and proportions of ingredients are the same as above:—

group. The other group had previously reacted with the OH groups of the polyester. Only 2.07 grams of diisocyanate, 50 that is 2.07 % of the initial polyester, remain.

#### EXAMPLE 2

A kneader of two litres capacity which has been heated up to 120° C. is charged 55 with 1000 parts of glycol adipic acid polyester of hydroxyl number 50 dehydrated in vacuum at 130° C. and 160 parts of 1,5 naphthylene diisocyanate are added. After about 10 to 15 minutes 22 60 parts of thiodiethylene glycol are added to the mix. Whereas before the addition of thiodiethylene glycol viscosity of the mix had scarcely changed, a great increase is now effected after a short time 65 and, about 20 to 30 minutes later, there is obtained a crumbly material which drops from the paddles of the kneader and can be made into a sheet. Press molding is performed at 150° C. and the following 70 figures are obtained:—

75	Tensile strength - - - - -	239.7 kg/cm <sup>2</sup>
	Elongation at break - - - - -	545 %
	Permanent set - - - - -	3 %
	Tear resistance - - - - -	125 kg/cm <sup>2</sup>
	Load at 300% elongation - - - - -	34 kg/cm <sup>2</sup>
	Hardness - - - - -	62 Shore degrees
	Resiliency - - - - -	69 % of height of fall attained by elastic rebound

other proportions of ingredients are the same as above:—

85	Tensile strength - - - - -	320 kg/cm <sup>2</sup>
	Elongation at break - - - - -	640 %
	Permanent set - - - - -	6 %
	Tear resistance - - - - -	158 kg/cm <sup>2</sup>
90	Load at 300% elongation - - - - -	35 kg/cm <sup>2</sup>
	Hardness - - - - -	60 Shore degrees
	Resiliency - - - - -	70 % of height of fall attained by elastic rebound

The material thus obtained is suitable for conveyor belts.

**EXAMPLE 3**

5 1000 parts of 1,2-propylene glycol-  
adipic acid polyester of hydroxyl number 50 are dehydrated at 130° C and 12 mm. pressure and are caused to react with 160

parts of 1,5-naphthylene diisocyanate. After completion of reaction 30 parts of triethylene glycol are added to 10 the mix at 130—135° C. Increase of viscosity is somewhat less than in the case of quinone. The soft material obtained after rolling and press molding exhibits the following properties:—

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Tensile strength - - - -	158 kg/cm <sup>2</sup>
Elongation at break - - - -	92%
Permanent set - - - -	12%
Tear resistance - - - -	37.5 kg/cm <sup>2</sup>
Load at 300% elongation - - - -	22 kg/cm <sup>2</sup>
Hardness - - - -	68 Shore degrees
Resiliency - - - -	41% of height of fall attained by elastic rebound

25 On applying the above material on cotton textiles or other fabrics, e.g. polyurethane fabrics coatings for collapsible boats are obtained which are distinguished by an excellent tensile strength and, above all, by a good resistance to 30 ageing

**EXAMPLE 4**

35 500 parts of a technical glycol adipic acid polyester of the OH-value 58 (corresponding to 1.75% OH) and of the acid value 1 which, after condensation, was blown with air at 130° C. for half an hour, are carefully dehydrated at the same temperature and in a vacuum of

12 mm. As soon as dehydration is completed which takes about one hour, 80 parts 40 of 1,5-naphthylene diisocyanate are added giving rise to an increase of temperature of 5 to 8° C. After completion of reaction 10 parts of 1,4-butene diol are added at 130° C. and, after shortly stirring, the 45 hot mix is cast into the mold. The mold is afterheated in a drying chamber at 100° C. whereby the mix becomes rubber-like after about half an hour. After further heating for 5 to 6 hours reaction 50 is completed and a material with rubber-elastic properties is obtained. A test resulted in the following figures:—

55

Tensile strength - - - -	281 kg/cm <sup>2</sup>
Elongation at break - - - -	720%
Permanent set - - - -	7%
Tear resistance - - - -	100 kg/cm <sup>2</sup>

60

Resiliency - - - -	60% of height of fall attained by elastic rebound
Hardness - - - -	73 Shore degrees

65 As moldings there may be mentioned plates, pipes, cylinders, rings, boots or parts of boots, balls, elastic structural parts for machines, coverings for ball mills and classifying apparatus.

70 The good abrasion is illustrated by the following test: two iron drums of 250 mm. length and 200 mm. diameter one of which is lined with a 2 mm. thick covering of the above material were filled each with 2000 grams of quartz pieces and rolled for 75 hours. After that time the iron drum with the above lining had lost 2 grams of its weight by abrasion whereas 75 the drum not lined had lost 12 grams. The powdered quartz obtained in the iron drum lined with the above material had a white colour whereas the powdered quartz in the other drum was grey owing 80 to the iron dust abraded by the rolling.

addition of 50 parts of carbon black as described in the foregoing examples and caused to react with 160 parts of 1,5-naphthylene diisocyanate at 130° C. After about 10 minutes, as soon as temperature 90

drops, 25 parts of quinone are added and, after shortly stirring, the mix is cast into a rotating drum heated up to 100° C. into the inside surface of which the profile of a bicycle tyre has been cut. The casting 95 mold may either be flat or hollow-shaped with a metal core so that tyres will be obtained which represent the final shape. Flat-cast tyres are shaped before after-heating on a straining tube or metal core. 100 After about 20 minutes the contents of the drum have solidified and, after further 40 minutes, the tyre can be taken out at 100° C. the tyre being then afterheated in a drying chamber for 5 to 6 hours at 105 the same temperature. Depending on the quantities of ingredients and the shape of the drum tyres of different sizes may be prepared, the following properties being obtained thereby:—

110

**EXAMPLE 5**

1000 parts of a glycol adipic acid polyester blown by air of hydroxyl number 52 (corresponding to 1.58% OH) and of the acid value 0.8 are dehydrated after the

5	Tensile strength - - - -	384 kg/cm <sup>2</sup>
	Elongation at break - - - -	600%
	Permanent set - - - -	3%
	Tear resistance - - - -	175 kg/cm <sup>2</sup>
	Resiliency - - - -	39% of height of fall attained by elastic rebound
	Load at 300% elongation - - - -	45 kg/cm <sup>2</sup>
	Hardness - - - -	67 Shore degrees

If glycol adipic acid polyester is substituted by a polyester mix composed of 700 parts of glycol adipic acid polyester and 300 parts of 1,2-propylene glycol adipic acid polyester the following properties are obtained:—

15	Tensile strength - - - -	235 kg/cm <sup>2</sup>
	Elongation at break - - - -	570%
	Permanent set - - - -	14%
	Tear resistance - - - -	117 kg/cm <sup>2</sup>
	Resiliency - - - -	47% height of fall attained by elastic rebound
20	Load at 300% elongation - - - -	54 kg/cm <sup>2</sup>
	Hardness - - - -	76 Shore degrees

#### EXAMPLE 6

1000 parts of glycol adipic acid poly-  
ester of hydroxyl number 52 correspond-  
ing to 1.58% OH, and of the acid value  
0.8 are mixed prior to dehydration with  
10 drops of concentrated hydrochloric  
acid and, thereafter, dehydrated as de-  
scribed above. After reaction with 160  
parts of 1,5-naphthylene diisocyanate 25  
parts of quinone are added and the mix  
is well stirred. Then 1.5 parts by volume  
of hexahydrodimethyl aniline are added  
while stirring and the mix is cast into the  
drum described above. 15 to 20 minutes  
later the tire can be removed from the  
mold and cured by afterheating at 100°  
C. for 5 to 6 hours.

#### EXAMPLE 7

1000 parts of glycol adipic acid poly-  
ester of hydroxyl number 52 (correspond-  
ing to 1.58% OH) and of the acid value  
0.8 which has been dried in the vacuum  
at 130° C. are caused to react with 210 parts  
of a nitrobenzidine diisocyanate while  
stirring. After completion of reaction 25  
parts of quinone are stirred into the mix  
at 130° C. which is then cast into the  
mold. By afterheating at 100° C. for 24  
hours rubberlike products with good  
mechanical properties are obtained.

#### EXAMPLE 8.

1000 parts of glycol adipic acid poly-  
ester dehydrated as described above with

90	Tensile strength - - - -	381 kg/cm <sup>2</sup>
	Elongation at break - - - -	625%
	Permanent set - - - -	12%
	Tear resistance - - - -	96 kg/cm <sup>2</sup>
	Load at 300% elongation - - - -	86 kg/cm <sup>2</sup>
95	Hardness - - - -	81 Shore degrees
	Resiliency - - - -	39% height of fall attained by elastic rebound

a hydroxyl content of 1.5% are caused  
to react with 232 parts of *o*-dichloro-  
benzidine diisocyanate at 130° C. Tem-  
perature drops to 118 to 120° C. and is  
raised again to 130° C. As soon as reac-  
tion between the polyester and the diiso-  
cyanate starts a rise of temperature to  
148 to 150° C is to be observed. While  
stirring it is cooled down to 140° C. and  
the mix is divided into three portions of  
300 parts each.

At 140° C. 7.5 parts of quinone are  
stirred into the first mix, 6 parts of 1,4-  
butylene glycol into the second mix and  
5.8 parts of butenediol into the third  
mix and all mixes are immediately cast  
into molds. By after-heating at 100° C.  
for 24 hours rubberlike products with good  
properties are obtained.

#### EXAMPLE 9

1000 parts of a carefully dehydrated  
glycol adipic acid polyester with  
hydroxyl number 52 (corresponding to  
1.58% OH) and of the acid value 1 are  
caused to react with 200 parts of 1,5-  
naphthylene diisocyanate at 130° C. while  
stirring and, after the rise of temperature  
is completed, 48 parts of finely powdered  
quinone are stirred into the mix at 135°  
C. After repeatedly stirring the mix is  
cast into molds and after-heated at 100°  
C. for 8 hours. The rubberlike material  
thus obtained exhibits the following  
mechanical properties:—

If 1000 parts of the dried glycol adipic acid polyester are caused to react in the same way as described above with 248 parts of 1,5-naphthylene diisocyanate and 74 parts of quinide (1,4-dihydroxycyclohexane), a material with the following mechanical properties is obtained:—

10	Tensile strength - - - - -	228 kg/cm <sup>2</sup>
	Elongation at break - - - - -	440%
	Permanent set - - - - -	18%
	Tear resistance - - - - -	96 kg/cm <sup>2</sup>
	Load at 300% elongation - - - - -	133 kg/cm <sup>2</sup>
	Hardness - - - - -	88 Shore degrees
15	Resiliency - - - - -	38% height of fall attained by elastic rebound

If 300 parts of 1,5-naphthylene diisocyanate and 100 parts of quinide are caused to react with the above glycol adipic acid 20 polyester a material with the following properties is obtained:—

25	Tensile strength - - - - -	234 kg/cm <sup>2</sup>
	Elongation at break - - - - -	370%
	Permanent set - - - - -	11%
	Tear resistance - - - - -	83 kg/cm <sup>2</sup>
	Load at 300% elongation - - - - -	130 kg/cm <sup>2</sup>
	Hardness - - - - -	84 Shore degrees
	Resiliency - - - - -	28% height of fall attained by elastic rebound

#### EXAMPLE 10

30 200 parts of a hexanediol-adipic acid polyester having a hydroxyl content of 1.55% are dehydrated and caused to react at 130° C. with 32 parts of 1,5-naphthylene-diisocyanate, reaction starting 35 immediately and temperature being raised thereby to 138—140° C. After completion of reaction and at a temperature of 135° C. 5 parts of hexanediol are added to the mix which is then cast into the mold. By after heating for 10 hours a 40 rubberlike material is obtained which exhibits the following properties:—

45	Tensile strength - - - - -	248 kg/cm <sup>2</sup>
	Elongation at break - - - - -	600%
	Load at 300% elongation - - - - -	110 kg/cm <sup>2</sup>
	Tear resistance - - - - -	121 kg/cm <sup>2</sup>
	Hardness - - - - -	86 Shore degrees
	Resiliency - - - - -	57% of height of fall attained by elastic rebound

#### EXAMPLE 11

50 A stirring vessel which is connected with a vacuum pipe line is charged with 150 parts of ethylene-glycol-adipic acid polyester having a hydroxyl content of 1.65% and a COOH content of 0.010% and 250 parts of propylene glycol adipic acid with an OH content of 1.42% and a COOH content of 0.12% and 35 parts of carbon black. The mix is evacuated at 130° C. 55 for 15 minutes. Thereafter, 20 parts of butadiene sulphone and 26 parts of paraffin are added. It is stirred at normal pressure at 140° C. and then the vessel is evacuated for 30 minutes. Now the mix 60 is caused to react with 165 parts of naphthylene-1,5-diisocyanate, temperature is decreased to 115° C. and chain-lengthening and cross-linking is carried out with 25 parts of molten quinide. After 15—25 65 minutes viscosity suddenly increases, the stirrer being blocked thereby. The non-sticking material which is easily hot-moldable is removed from the vessel, cold 70 rolled and extruded into bicycle tubes at 50—100° C. The material is distinguished by an especially low permeability to gas 75 which is essentially lower than in the case of natural rubber or synthetic rubber-like materials on the basis of butadiene. Tear resistance of tubes thus prepared is so good that the hole for introducing the valve need not be reinforced in any way. The roughened tube ends are welded by a solution of natural rubber or of synthetic rubberlike materials to which, before application, some p,p',p"-triphenylmethane-tri-isocyanate has been added; welding can also be performed by means of the uncured material itself prepared as described above. In the latter case the mix which, preferably, is diluted with a solvent is immediately applied as welding agent after the addition of quinide. The tubes thus prepared exhibit the following properties:—

Tensile strength - -	420 kg/cm <sup>2</sup>
Elongation at break - -	600%
Permanent set - -	10%
Tear resistance - -	35 kg/cm <sup>2</sup>

## 5      EXAMPLE 12

The mix of glycol adipic acid polyester, propylene glycol adipic acid polyester and carbon black prepared as described in Example 11 is homogenized on the roller and, after putting it into an open vessel, a stream of air is bubbled therethrough at 140° C. for 1—1½ hours. 165 parts of naphthylene-1,5-diisocyanate are then added, heating 15 is stopped and the isocyanate polyester is cooled down to 115° C., and 25 parts of esterified montan wax and 20 parts of butane diol-1,4 are added while vigorously stirring. The reaction mix is cast upon 20 waxed and well dried plates which are put into a drying chamber of a temperature of 115° C. Condensation is carried through until the desired degree of plasticity is achieved. After 30—60 minutes 25 the plastic material can be removed from the plates. The material is then cut into strips and without rolling extruded into a water hose by means of a heated extruding machine. The product thus extruded 30 is stored at room temperature for 48 hours and then afterheated at 100° C. for 12 hours the properties obtained being the following:—

Tensile strength - -	310 kg/cm <sup>2</sup>
Elongation at break - -	590%
Tear resistance - -	29 kg/cm <sup>2</sup>

Fabric lining which is usually required for water hoses can be dispensed with owing to the high tensile strength and resistance to ageing of the products prepared as described above. The condensate may easily be extruded into threads. Such threads are first stored at room temperature for 24 hours and then afterheated at 45 100° C. A single thread exhibits a tensile strength of 5 kg/mm<sup>2</sup> and an elongation at break of 600%.

## EXAMPLE 13

1000 parts of a propylene glycol adipic acid polyester having a hydroxyl content of 1.5% and a COOH content of 0.15% are homogenized in the grinding mill and subjected to reduced pressure in a vessel at 130° C. and 12 mm. pressure for 30 50 minutes. 10 parts of paraffin and 0.2 part by volume of concentrated hydrochloric acid are added and the whole is subjected to reduced pressure once more for 20 minutes. Now the mix is caused to react 55 with 164 parts of naphthylene-1,5-diisocyanate and then cooled down to 110° C. Thereafter a mixture of 18.4 parts by weight of butane diol-1,4 and 2.5 parts of glycerine- $\alpha$ -phenylether is stirred into

the mix. After 45 minutes the material is 65 removed from the vessel and, on a cold roller, 10 parts of esterified lower fatty acids from paraffin oxidation are added to the mix which is then extruded by means of a heated extruding machine. The 70 properties of the material thus condensed are as follows:—

Tensile strength - -	210 kg/cm <sup>2</sup>
Elongation at break - -	560%
Tear resistance - -	17 kg/cm <sup>2</sup>

## EXAMPLE 14

500 parts of a propylene glycol adipic acid polyester having a hydroxyl content of 1.25%, and a COOH content of 0.12% and 500 parts of ethylene glycol adipic acid polyester having an OH content of 1.62% and a COOH content of 0.10% are subjected to reduced pressure while stirring at 130° C. for 20 minutes by means of a water-jet suction pump. 0.13 85 part by volume of concentrated hydrochloric acid is added and the mix is again subjected to reduced pressure for 30 minutes. Now the mixed polyester is 90 caused to react with 160 parts of naphthylene-1,5-diisocyanate for 7 minutes and the mix is evacuated once more.

The batch is divided into 2 equal portions. 12.5 parts of quinone are stirred into one portion (580 parts) and the mix 95 is cast upon a plate previously heated up to 100° C. and, for securing an easy removal of the material, provided with a protective coating of paraffin or of an aqueous solution of the condensation product from a fatty acid chlorine and methyl taurine. After one hour the bubble-free sheet thus obtained is removed from the plate and afterheated at 100° C. for 3 hours. The remaining 105 portion of the above mix is dissolved with 200—4500 parts by volume of a well dried organic solvent, such as methylene chloride, benzene or acetic acid ester. For curing 10 parts of 1—4 butanediol are 110 stirred into the solution. It can be used for preparing dipped articles or extruded from a cylinder. After 24 hours the products thus prepared are afterheated at 100° C. for 1—4 hours, the properties 115 obtained being the following:—

Tensile strength - -	320 kg/cm <sup>2</sup>
Elongation at break - -	650%
Tear resistance - -	27 kg/cm <sup>2</sup>

## EXAMPLE 15

120 A bicycle tyre of 1200 grams prepared by means of the centrifugal casting process in accordance with Example 5 which has become useless on account of a puncture or a crack is reclaimed and made into 125 a sheet by passing it through a pair of cold friction rollers at a narrow and, later

on, a wider space. The sheet is divided into 2 equal portions.

To one portion there are added on the roller 60 grams of an ethylene glycol phthalic acid polyester with hydroxyl number 30 and the acid value 5. Under a pressure of 30 kg/cm<sup>2</sup> and at a temperature of 150° C. for 15 minutes this mix is made into heels which as to durability 10 and wearing properties are superior to other material, such as leather or rubber. The second portion of the sheet is directly worked up without additional compounds. Heels made thereof also exhibit very good 15 wearing properties and have a good durability.

35	Tensile strength - - - - -	183 kg/cm <sup>2</sup>
	Elongation at break - - - - -	700%
	Load at 300% elongation - - - - -	46 kg/cm <sup>2</sup>
	Permanent set - - - - -	21%
	Resiliency - - - - -	50% of height of fall attained by elastic rebound at 20° (60% at 70° C.)
40	Hardness - - - - -	60 Shore degrees
	Tear resistance - - - - -	83 kg/cm <sup>2</sup>

Plates thus prepared, sections of which 45 may possess a shaped profile, are extremely suitable as floor covering material which is exposed to high stresses for instance, in railway-cars, street cars etc.

50 The reclaiming process described above can also be carried out with a mixture of scrap derived from a propylene glycol adipic acid polyester with scrap of ethylene glycol adipic acid polyester or of a mixed ester of adipic acid with ethylene glycol and 1,2-propylene glycol or of mixes of ethylene glycol adipic acid polyester with 1,2-propylene glycol polyester.

60 Scrap of the kind as described in Example 15 and Example 16 can also be converted into moldable sheets after mixing same with very finely crushed and ground scrap of such rubber-like 65 material of the polyester series as are cured with water or hydrogen sulphide instead of with bifunctional organic compounds.

95	Tensile strength - - - - -	300 kg/cm <sup>2</sup>
	Elongation at break - - - - -	600%
	Load at 300% elongation - - - - -	80
	Permanet set - - - - -	25%
	Resiliency - - - - -	60% of height of fall attained by elastic rebound
	Hardness - - - - -	72 Shore degrees

#### EXAMPLE 18

1000 parts of glycol succinic acid polyester of hydroxyl number 50 (corresponding to 1.5% OH) are dehydrated in a

#### EXAMPLE 16

Scrap of the reaction product of a linear propylene glycol adipic acid polyester of hydroxyl number 50 with 1,5-naphthylene diisocyanate + hexahydriodiphenyl ether containing 5% by weight of carbon black are thoroughly mixed on the roller with 10% of an incompletely cured condensation product consisting of the same 25 ingredients and having been stored for some days. This mix is made into a sheet on the roller. Pressing into plain 4 mm thick plates is performed at 150° C. for 10 minutes and under a pressure of 30 30 kg/cm<sup>2</sup>.

The mechanical properties of the products thus reclaimed exhibit the following figures:—

	183 kg/cm <sup>2</sup>
	700%
	46 kg/cm <sup>2</sup>
	21%
	50% of height of fall attained by elastic rebound at 20° (60% at 70° C.)
	60 Shore degrees
	83 kg/cm <sup>2</sup>

The following products are mentioned which can be obtained in accordance with 70 the above process: boot soles, leather substitute, packing rings, rubber buffers etc.

#### EXAMPLE 17

Scrap of the reaction product from linear ethylene glycol adipic acid polyester of hydroxyl number 50 and 1,5-naphthylene diisocyanate which has been cured with a glycol according to the invention is ground and heated in an autoclave under steam pressure (4—15 atmospheres excess pressure) for 30—90 minutes, a strongly adhesive material being obtained after drying which can be made into a sheet on the roller. By further incorporating therewith 5—10 parts 85 of a naphthylene diisocyanate and 1—2 parts of butylene glycol (calculated on 100 parts of the reaction product) and on press moulding into, for instance, 4 mm thick plates (30°/130° C. at 50 kg/cm<sup>2</sup>) 90 products are obtained which exhibit the following properties:—

	300 kg/cm <sup>2</sup>
	600%
	80
	25%
	60% of height of fall attained by elastic rebound
	72 Shore degrees

stirring vessel at a temperature of 130° C. and under a pressure of 12 mm. The 105 polyester is free from water as soon as formation of bubbles ceases. While stir-

ring 160 parts of 1-5 naphthalene diisocyanate are added at 130° C., a rise of temperature to 142° C. being observed. As soon as the temperature falls, 25 parts of finely powdered quinone are stirred into the mix. After a few minutes the mix becomes more and more viscous, and, at last, the viscosity increases to such an extent that 20 minutes later the stirrer is stopped owing to the material having been converted into a crumbly mass.

The condensation product thus obtained represents at room temperature a leather-like material which is converted into a highly elastic state only at elevated temperatures (60° C.-80° C.).

British Patent Specification 553,733 claims the process for the manufacture of high molecular weight polymers which 20 comprises heating an organic polyisocyanate or polyisothiocyanate with a low molecular weight linear polymer produced from ingredients comprising a dibasic carboxylic acid or an ester-forming derivative of such an acid, at least one complementary bifunctional esterifiable compound (at least one function being an alcoholic hydroxyl group), and optionally one or more additional bifunctional compounds, until a polymer of substantially higher molecular weight is formed.

What we claim is:-

1. The process of producing elastomeric products which comprises reacting a dehydrated organic linear polyester of OH value between about 20 and about 80 made from at least one saturated dicarboxylic acid or hydroxy carboxylic acid, optionally in mixture with a small amount of 35 an aromatic or an unsaturated dicarboxylic acid, and at least one glycol optionally in mixture with a small amount of a polyfunctional amine or an amino alcohol, with an amount of organic diisocyanate such that there is an excess of 40 20-250 per cent. of NCO groups over the number which is necessary for combining with the OH groups of the polyester, intermixing with the isocyanate-modified polyester thus formed a non-polymeric and non-formaldehyde-liberating glycol in such a proportion that the 45 excess of free NCO groups will after reac-

tion with the glycol, be reduced to an amount which represents an amount of 55 diisocyanate which is by weight at most 4 per cent. of the weight of the initial polyester, and reacting the glycol with the isocyanate-modified polyester while moulding the mixture. 60

2. Process as claimed in claim 1 in which the organic diisocyanate is an aromatic diisocyanate.

3. Process as claimed in claim 1 in which the organic diisocyanate is an 65 aromatic polycyclic diisocyanate.

4. Process as claimed in claim 1 in which the organic diisocyanate is naphthalene-1,5-diisocyanate.

5. Process as claimed in any of claims 70 1-4 in which the organic linear polyester has 1.2-1.8% by weight of OH groups.

6. Process as claimed in any of claims 1-5 in which the glycol mixed with the isocyanate-modified polyester is 1,4-buty- 75 leneglycol.

7. Process as claimed in any of claims 1-5 in which the glycol mixed with the isocyanate-modified polyester is quinone.

8. Process as claimed in any of claims 80 1-7 in which the initial reaction is performed in the presence of an acid reacting agent.

9. Process as claimed in any of claims 1-8 in which the reaction initiated by 85 incorporation of the glycol is effected in the presence of an alkaline reacting agent.

10. Process as claimed in claim 9 in which the alkaline reacting agent is a ter- 90 tiary amine.

11. Process as claimed in any of the preceding claims in which the organic linear polyester is one that has been blown with an inert gas at raised temperature. 95

12. Process for the manufacture of moulded products substantially as described in any of the examples.

13. Moulded products produced by a process as claimed in any of the preceding claims. 100

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